THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS CONTAINING ORGANIC MOLECULES

BY

ALLAN DALE GOTT

B.S., The University of the South, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS

1952

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS CONTAINING ORGANIC MOLECULES

BY

ALLAN DALE GOTT

B.S., The University of the South, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS

1952

ACKNOWLEDGMENT

It is a pleasure to express sincere appreciation for the guidance and consideration of Dr. John C. Bailar, Jr. who instigated and directed this investigation. The author is also deeply grateful for the patience, encouragement and helpfulness of his wife during his graduate study.

THE STEREOCHEMISTRY OF COMPLEX INORGANIC COMPOUNDS CONTAINING ORGANIC MOLECULES

Introduction

There is considerable evidence (1,2) to support the theory that in a complex ion containing optically active ligands, the more stable and more symmetrical form of the complex is the one in which all of the optically active groups have the same sterical configuration. It seems reasonable to assume, therefore, that some "selectivity" would be exhibited in the introduction of an optically active molecule or ion into a coordination sphere which contains other coordinated groups of like configuration.

A great amount of evidence has been obtained in this laboratory for the selectivity of this type of reaction (3,4,5,6). The resolution of *racemic*-tartaric acid, begun in earlier years (4,5), has now been extended and the resolution of *racemic*-mixtures of organic acids containing one asymmetric carbon atom has been developed.

Experimental And Discussion

The partial resolution of *racemic*-tartaric acid by the reaction of excess *levo*- propylenediamine with *racemic*-tartrato-*bis*-*levo*-propylenediamine cobalt (III) chloride was reported by Jonassen (4). This resolution was repeated, but under different experimental conditions than those previously reported. Conclusive evidence was obtained to indicate that the complex containing the *dextro*-tartrate ion was more stable than the complex containing the *levo*-tartrate ion, since the latter was much more readily liberated from the coordination sphere by the action of the *levo*-propylenediamine on the tartrato complex.

Attempts were made to establish the difference in stability of the *dextro*-tartrato-*bis*-*levo*-propylenediamine cobalt (III)

complex and the *levo*-tartrato-*bis*-*levo*-propylenediamine cobalt (III) complex by a spectrophotometric study of the reaction rates of the individual complexes with excess *levo*-propylenediamine. The results obtained were inconclusive, because the high absorption of the complexes involved in the reaction necessitated working with very dilute solutions. However, some insight into the course of the reaction was obtained. It is apparent that "hydroxolation" took place, with the formation of a hydroxo-tartrato-*bis*-*levo*-propylenediamine cobalt (III) complex. The reaction does not proceed to the complete liberation of the tartrate ion and the formation of the *tris*-*levo*-propylenediamine cobalt (III) ion unless a large excess of *levo*-propylenediamine is present in a highly concentrated solution.

The method of resolution of *racemic*-tartaric acid proposed by Hamilton (5) was also investigated. Since some difficulty had been encountered in attempts to verify Hamilton's results (6), a slightly different procedure was employed.

A solution containing the carbonato-complex and a 100% excess of *racemic*-tartaric acid was evaporated to dryness on the steambath and subsequently oven-dried for four days at 90°C to insure complete reaction of the tartrate ion. When this somewhat powdery mass was dissolved in a small amount of water and a large excess of a saturated solution of barium hydroxide added, the uncoordinated tartrate fraction was precipitated as barium tartrate and removed by filtration. Sufficient excess of barium hydroxide remained in the filtrate to effect complete precipitation of the preferentially coordinated tartrate fraction upon standing for about four days.

The results of the partial resolution indicated that more than a one-hundred percent excess of barium hydroxide was necessary to effect complete precipitation of the "uncoordinated" tartrate fraction. This observation was also reported by Hamilton (5), who concluded that the *levo*-tartrate ion must be attached to the central cobalt (III) ion as well as the more firmly coordinated *dextro*-tartrate ion. This would

necessitate either monodentate coordination of both the *dextro*- and *levo*-tartrate isomers, the former being more firmly held, or a coordination number greater than six for the central cobalt (III) ion.

Even though only eight percent resolution was obtained, the experiment lends considerable support to the utilization of "preferential coordination" as a means of resolving *racemic*- mixtures of organic acids.

The possibility of resolving *racemic*- mixtures of organic acids which contain one asymmetric carbon atom and which are monodentate coordinating agents, by the method of preferential coordination, was intriguing. The resolution of *racemic*-lactic acid by the usual methods is very tedious and the resolutions of *racemic*-α-chloropropionic acid and *racemic*-α-bromopropionic acid have received very little attention. It was desirable to develop a perfectly general procedure for the resolution of these three acids by preferential coordination. Since all common salts of these three acids are quite soluble or tend to decompose in water, the acids were recovered by extraction with ether.

A mixture of a one-hundred percent excess of the *racemic*- acid and a carbonate solution of carbonato-*bis-levo*-propylenediamine cobalt (III) complex was evaporated to dryness. The residue was then dissolved in a small amount of water and the uncoordinated acid extracted with ether. An aqueous solution of the extracted acid was prepared by evaporating the ether on a steambath. In order to recover the fraction of the acid which had entered the coordination sphere it was necessary to decompose the complex by sodium sulfide, remove the precipitated cobalt sulfide by filtration, acidify with sulfuric acid, and extract with ether. The acid fractions recovered in this way were optically active.

Both *racemic*-lactic acid and *racemic*-α-chloropropionic acid were resolved to an extent of greater than thirty percent by this procedure. The partial resolution of α-bromopropionic acid was studied only qualitatively since the specific rotation

of the pure optically active acid is not known. The results obtained are significant and are of both theoretical and applied interest, since the procedure employed is much simpler than the usual method of alkaloid salt recrystallizations and could be adapted to a much larger scale than is possible with enzymatic resolutions.

The selectivity of this type of reaction is valuable in determining the sterical configuration of optically active isomers of organic molecules. In the resolutions of *racemic*-tartaric acid, *racemic*-lactic acid, and *racemic*-α-chloropropionic acid it was always the *dextro*- form of the acid which preferentially entered the coordination sphere, even though the *dextro*- forms of the latter two are levorotatory whereas *dextro*-tartaric acid is dextrorotatory. The *dextro*- forms of these acids must then have the same configuration as *levo*-propylenediamine, as proposed by Jonassen (4).

Conclusions And Summary

The partial resolution of *racemic*-tartaric acid by the reaction of excess *levo*-propylenediamine with *racemic*-tartrato-*bis* -*levo*-propylenediamine cobalt (III) chloride in aqueous solution, which was achieved by Jonassen (4), was repeated under a variety of conditions. Some insight into this reaction in dilute solution was obtained. The method of partial resolution of *racemic*-tartaric acid by "preferential coordination" as developed by Hamilton (5) was also investigated and the procedure improved. Several factors affecting the rotation of optically active tartaric acid were determined.

A general procedure for the partial resolutions of *racemic*-lactic acid, *racemic*-α-chloropropionic acid, and *racemic*-α-bromopropionic acid was developed. A greater than thirty percent resolution of both *racemic*-lactic acid and *racemic*-α-chloropropionic acid was achieved.

At present it is not possible to explain why the reactions involving coordination by optically active groups are selective, especially in the case of monodentate groups. It is entirely

possible that a coordination number greater than six for the central cobalt (III) ion is involved but further study is necessary to confirm this supposition. The results of these investigations are of both theoretical and practical importance and provide a basis for future studies.

BIBLIOGRAPHY

1. Smirnoff, Helv. Chim. Acta., 3, 177 (1920).
2. Hürliman, Dissertation; Jaeger, "Optical Activity and High Temperature Measurements," pp 167-168, McGraw-Hill, N.Y. (1930).
3. Stiegman, Thesis, University of Illinois, 1937.
4. Jonassen, Thesis, University of Illinois, 1946.
5. Hamilton, Thesis, University of Illinois, 1947
6. Sister Martinette, Thesis. University of Illinois, 1949.

VITA

The author was born in Cleveland, Ohio, on July 28, 1923. Soon afterwards his family moved to Chattanooga, Tennessee, where he was educated in the public schools, graduating from Chattanooga High School in June, 1941. He entered the University of the South at Sewanee, Tennessee, in September, 1941, and completed two years of undergraduate study before being called into the Weather Service of the Army Air Force in March, 1943, at the University of North Carolina. He received his commission at the University of Chicago in June, 1944, and was separated from the Service in June, 1946, with the rank of 1st Lieutenant. He returned to the University of the South in September, 1946, and received the degree of Bachelor of Science in Chemistry in June, 1948. He was awarded the Rouge Scholarship in his junior year and was the Salutatorian of his college graduating class. He entered the Graduate College of the University of Illinois in the fall of 1948, and held an appointment as a half-time teaching assistant in inorganic chemistry from that date until graduation in February, 1952. The degree of Master of Science in Chemistry was received in August, 1949.

The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Phi Beta Kappa, and Phi Gamma Delta.